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MICROSTRUCTURE OF DIMETHYLSILOXANE BASED MAGNETIC ELASTOMERS

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Микроструктура магнитных эластомеров
на основе диметилсилоксана

Исследованы эластомеры на основе диметилсилоксана, допированные двумя типами магнитных частиц (нано- и микроразмерными). Получено, что добавление Fe_3O_4-наночастиц и применение магнитного поля во время процесса полимеризации приводят к существенному изменению локальной структуры эластомера. Полимер, допированный Fe_3O_4-наночастицами, представляет собой специфическую структуру массовых фракталов. Характерный размер массовых фракталов уменьшается в магнитном эластомере, полимеризированном в магнитном поле. Для эластомера, допированного большим количеством микрочастиц Fe (75%-я концентрация частицы), обнаружен эффект текстурирования; для образцов, полимеризированных в магнитном поле, этот эффект больше. Для всех концентраций микрочастиц получена размерность поверхностных фракталов.

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Microstructure of Dimethylsiloxane Based Magnetic Elastomers

Dimethylsiloxane based elastomers filled with two types of magnetic particles (nano- and micro-sized) were investigated. It was obtained that doping with Fe_3O_4 nanoparticles and applying of magnetic field during the polymerization process leads to a significant change of the local structure of elastomer. After filling the polymer with Fe_3O_4 nanoparticles the magnetic elastomer presents a mass fractal structure. The mass fractal dimension is decreasing in the magnetic elastomer polymerized in magnetic field. For the elastomer filled with a large amount of Fe microparticles (75% particle concentration) a texture effect is detected; for the samples polymerized in magnetic field the texture effect is higher. Surface fractal property is obtained for all microparticle concentrations.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

The interest in rubber-like smart active material devices in recent years stimulates an increasing number of efforts in both basic and applied research aspects for new elastomer technology. Magnetic elastomers belong to a specific class of so-called smart materials because they can respond to changes in their environment. They are composed of magnetic particles and a low-permeability matrix (Fig. 1). Applying an external magnetic field, a structure will be formed inside the material, or the structure embedded in the material will be changed.

Finely divided filler particles have been used for many decades as reinforcing agents in elastomers and their effect on the resulting macroscopic elastic properties was traditionally used in tires, seals and passive damping devices.

Combination of magnetic and elastic properties leads to different phenomena which are exhibited in a variable magnetic field [1–7]. It opens new possibilities for technological applications as: (1) magnetoelastic composite with particles made of magnetostrictive hard or soft ferromagnetic material; (2) magnetorheological elastomers for application in airplane and car industries as actuators or antifriction components; (3) heat-shrinkable elastic ferromagnets with variable magnetic and conductive properties.

Other applications that utilize magnetic polymer nanocomposites are currently emerging at a high rate. Examples include magnetic actuation in microelectro-

Fig. 1. Example of magnetic elastomers samples

mechanical systems (MEMS) and medical devices, thermal actuation through electromagnetic power harvesting, and magnetically actuated morphing structures.

The magnetoelastic properties of composites are not the bare sum of the elasticity of the polymer and the stiffness and magnetic properties of the filler, but are the result of a complex synergy of several effects, referring to different length scales and detectable by different techniques.

Many studies of the observed reinforcing effect from magnetic fillers have approached the problem from a magnetomechanical point of view and investigated the microscopic properties through the study of the magnetoelastic responses of the composite [1–4]. Less well understood, however, is the effect of the polymer-filled interaction with the local distribution of polymer around filler on a micro/nano length scale.

Such length scales are ideally suited for small-angle scattering investigations [8–10].

In this paper, the variation of the magnetic elastomer microscopic properties, due to the polymer matrix filling with two types of magnetic particles, (i) magnetite nanoparticles and (ii) Fe microparticles, is investigated by means of XRD, SANS and SAXS methods.

1. EXPERIMENTAL

Two types of samples were prepared at the Department of Electricity and Magnetism, West University of Timisoara [11–13]. One type was obtained with ferrofluid and was composed of oil based 7.7% particle volume concentration Fe_3O_4 ferrofluid with oleic acid as surfactant (Fig. 2) [14, 15], embedded in a polymer matrix formed from dimethylsiloxane, dibutyltindilaurate benzyl silicate, polymerized in zero field (sample A) or in an applied magnetic field of $B = 135.9$ mT (sample B). For the other type in the same polymer matrix Fe microparticles were embedded, obtained by thermal decomposition of $Fe_2(CO)_9$ (Fig. 3). In this case the polymerization process was performed in zero field and in an applied magnetic field $B = 156.5$ mT.

From electron microscopy images of Fe_3O_4 ferrofluid (Fig. 2) and of Fe particles obtained by thermal decomposition of $Fe_2(CO)_9$ (Fig. 3) and size-distribution histograms a mean radius of $\langle R \rangle = 5.7$ nm and a standard deviation of $\sigma = 1.94$ nm, and a mean diameter of $\langle D \rangle = 2.24$ μm and a standard deviation of $\sigma = 0.33$ μm were obtained.

In order to determine the phase composition, lattice microdistortions and average size of coherent length (average size of mosaic blocks), the samples were investigated by XRD, using DRON diffractometers: magnetite samples with CoKα radiation (National Institute of Research and Development for Technical

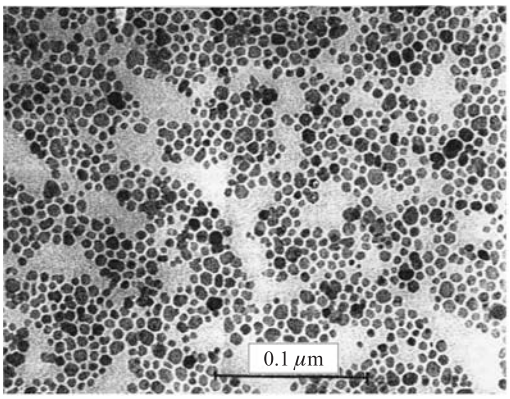

Fig. 2. Electron microscopy image of Fe_3O_4 particles in ferrofluid sample

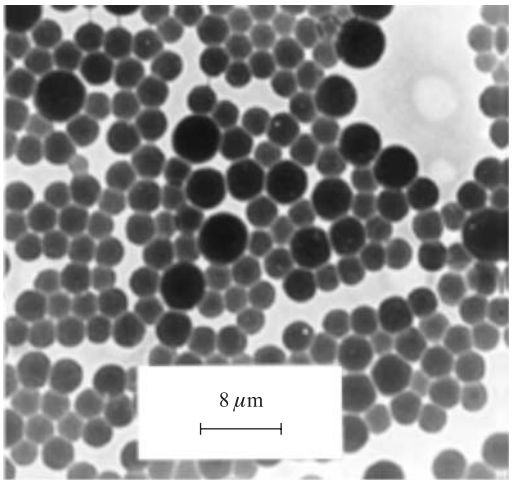

Fig. 3. Electron microscopy image of iron microparticles in mineral oil

Physics, Iasi), Fe doped samples with MoKα radiation (Polytechnic University of Timisoara), XRD data were handled using Ceck Cell and Rietveld software.

The samples were studied using small-angle X-ray (SAXS) and neutron (SANS) scattering methods. The SAXS experiments were performed at Rigaku spectrometer, using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002). The camera was equipped with a multiwire, gas-filled area detector with an active

area diameter of 20 cm. Two experimental setups were used to cover the q range of 0.007–1.1 Å^{-1}.

The SANS experiments were carried out on the YUMO diffractometer [16] at the IBR-2 pulsed reactor, JINR, Dubna, in the q range of about 0.006–0.3 Å^{-1}.

2. RESULTS

2.1. Magnetic Elastomers with Nanoparticles. From XRD data it results that the elastomer was doped with Fe_3O_4 particles about 10 nm average size, the elastomers contain practically the same concentration of Fe_3O_4, but with different average size of coherent blocks and microstrains. It was established that both samples contain a small amount of foreign phase (Fig. 4).

Data concerning SAXS measurements indicated a strong difference of the structure of samples doped and undoped with Fe_3O_4 particles. We have observed the systematic appearance of a Bragg diffraction peak in SAXS plots in the large region of q values (near $q = 0.9$ Å^{-1}; see Fig. 5).

Doping with Fe_3O_4 particles leads to a significant change of the local structure of elastomer, meaning the decrease of the quasi-crystalline phase concentration (see Fig. 3) and average size of the crystalline blocks (see Table 1). Apparently, from the fitting of the observed maximum corresponding to $q \approx 0.9$ Å^{-1} with a Pseudo-Voigt profile function it results that the elastomer is fragmented into small particles. The average size of elastomer blocks and the ordering distance decrease when magnetic field is applied during the polymerization process (see Table 1).

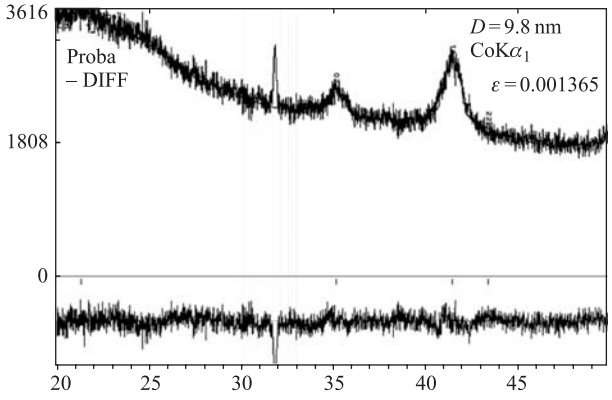

Fig. 4. Observed and calculated diffractograms (upper-side); difference between observed and calculated diffractograms (bottom-side) for Fe_3O_4 particles

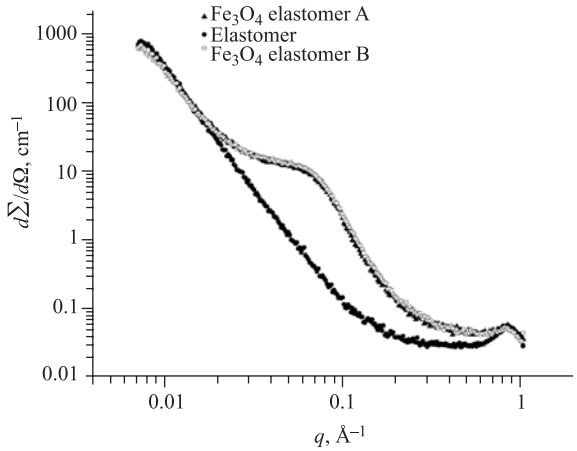

Fig. 5. SAXS experimental curves from samples A, B and simple elastomer obtained at Rigaku spectrometer in function at the Institute of Macromolecular Compounds, Prague [14]

Table 1. Variation of gravity center position (θ), average size of crystalline blocks (Δ) and ordering distance (D) in the elastomer matrix

Sample	θ	Δ, nm	D, nm
Elastomer matrix	11.56 ± 0.02	2.73 ± 0.04	0.763 ± 0.002
Elastomer with Fe_3O_4 particles (polymerization without magnetic field)	11.71 ± 0.01	2.38 ± 0.13	0.756 ± 0.001
Elastomer with Fe_3O_4 particles (polymerization with magnetic field)	11.41 ± 0.05	2.73 ± 0.14	0.775 ± 0.007

The maxima observed at $q \approx 0.08$ Å^{-1} (Fig. 5) correspond with the presence of about 100 Å sized nanoparticles, in agreement with the results of Klokkenburg et al. [17].

The SANS scattering intensities of dimethylsiloxane based polymer matrix reveal a power-law behavior as $I(q) \approx q^{-\alpha}$, with the exponent $\alpha < 4$. In the present case, when $\alpha < 4$, the fractal dimension is given by the formula $D_s = 6 - \alpha$ [18]. Consequently, the polymer matrix exhibits the behavior of a surface fractal object with a fractal dimension $D_s = 2.47 \pm 0.01$. After introducing the ferrofluid, the obtained magnetic elastomer became a mass fractal object with a mass fractal dimension $D_m = 2.91 \pm 0.01$ (Fig. 6).

In the case of SAXS experimental curves, the following results are obtained: (i) for the polymer matrix a surface fractal dimension is $D_s = 2.52 \pm 0.01$;

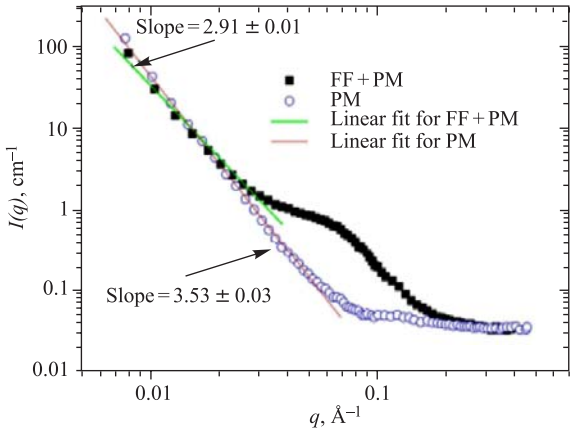

Fig. 6. Scattering intensity experimental curves and linear fits for polymer matrix (PM) and polymer matrix with embedded Fe_3O_4 ferrofluid (FF+PM) [8]

(ii) the elastomer with Fe_3O_4 ferrofluid presents a mass fractal dimension of $D_m = 2.93 \pm 0.01$;
(iii) the elastomer with Fe_3O_4 ferrofluid polymerized in magnetic field presents a mass fractal dimension of $D_m = 2.83 \pm 0.01$.

2.2. Magnetic Elastomers with Fe Microparticles. From XRD diffractograms of elastomers with Fe microparticles (in various concentrations) the relative intensities for different lattice planes with the variation of Fe concentration and of the polymerization magnetic field were obtained (Fig. 7). The principal maxima were attributed to Fe (b.c.c). Small maxima, near (110) of b.c.c phase, can be attributed to a f.c.c austenite-type structure.

In Table 2 the variation of relative intensities for different lattice planes with the variation of Fe microparticles concentration and polymerization magnetic field is presented. The relative intensities corresponding to the lattice planes (200), (211), (220) and (310) decrease for the samples synthesized without magnetic field, with Fe concentration until 50% Fe. For 75% Fe, the relative intensities of (200), (211), (220) decrease, while the relative intensity of (310) maxima increases. A small texture effect can take place for a larger Fe amount in the sample. For the samples polymerized in magnetic field a general decrease of relative intensities was observed, concerning (200) and (211) maxima, that means that the texture effect is higher due to a relative better orientation of Fe particles: magnetic field enhances the orientation of the samples as the (110) planes become perpendicular on magnetic field.

The SANS scattering intensities of dimethylsiloxane based polymer matrix with Fe microparticles reveal also a power-law behavior as $I(q) \approx q^{-\alpha}$, with

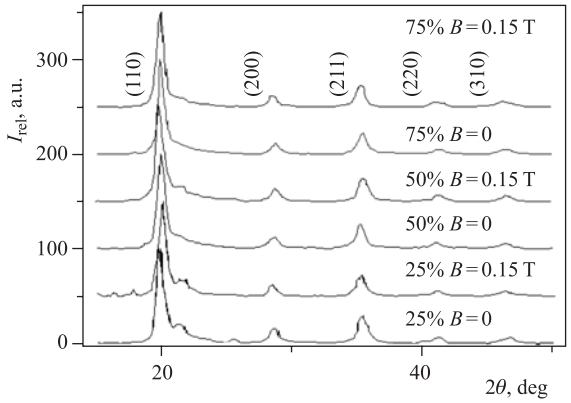

Fig. 7. Diffractograms of elastomers with Fe microparticles (in various concentrations) by using MoKα radiation

Table 2. Modification of relative intensities for different lattice planes with the variation of Fe microparticles concentration and polymerization magnetic field

Fe concentration, %	Relative intensities (MoKα)				
	(110)	(200)	(211)	(220)	(310)
$B = 0$					
25	100	14.4	26.4	5.8	9.9
50	100	12.5	21.6	5.0	7.9
75	100	13.7	28.3	8.9	8.3
$B = 0.15$ T					
25	100	9.2	22.5	4.4	5.5
50	100	11.6	24.8	7.3	5.5
75	100	8.7	18.1	6.0	12.2
Fe standard	100	15	26.5	3.9	8.7

the exponent $3 < \alpha < 4$ (Fig. 8). It was obtained for elastomer samples with 25% Fe particles concentration a surface fractal dimension of $D_s = 2.27 \pm 0.01$ for 50%, $D_s = 2.18 \pm 0.01$ and $D_s = 2.13 \pm 0.01$ for 75% Fe particles concentration.

For the scattering intensity of Fe particles a power-law behavior is obtained with an exponent of $\alpha = 4$, showing the particles to be smooth. In this case, using the Porod law $I = \frac{2\pi\rho^2}{q^4}S$, where S is the mean specific surface of the particles, a mean radius for Fe particles of $\langle R\rangle = 2.00 \pm 0.25$ μm is obtained in very good agreement with scanning electron microscopy data.

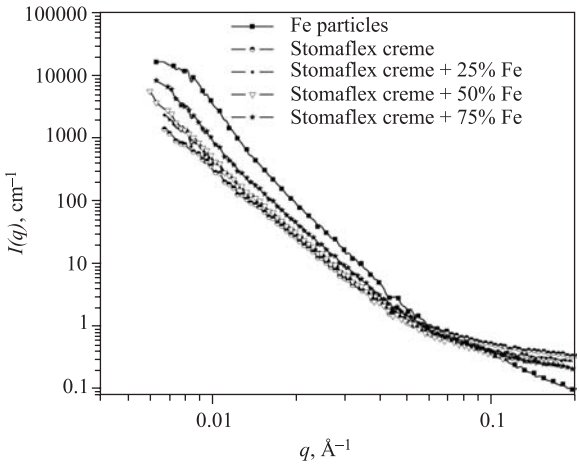

Fig. 8. SANS experimental curves of elastomer with Fe microparticles, stomaflex elastomer matrix and Fe particles

CONCLUSIONS

Dimethylsiloxane based elastomers filled with two types of magnetic particles (nano- and micro-sized) were investigated.

It was obtained that doping with Fe_3O_4 nanoparticles and applying of magnetic field during the polymerization process leads to a significant change of the local structure of elastomer. The decrease of the quasi-crystalline phase concentration, of the average size of the crystalline blocks and of the ordering distance is present.

The stomaflex polymer matrix is characterized as a surface fractal with a dimension of about $D_s = 2.52 \pm 0.01$. After filling the polymer with Fe_3O_4 nanoparticles the magnetic elastomer presents a mass fractal structure. The mass fractal dimension is decreasing in the magnetic elastomer polymerized in magnetic field.

For the elastomer filled with a large amount of Fe microparticles (75% particle concentration) a texture effect is detected; for the samples polymerized in magnetic field the texture effect is higher. Surface fractal property is obtained for all microparticle concentrations.

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